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ON THE TRANSFORMATION OF PICRIC ACID INTO PICRAMIC ACID, AND THE DETECTION OF GRAPE SUGAR

[Ueber die Umwandlung der Pikrinsäure in Pikraminsäure und über die Nachweisung des Traubenzuckers]

by

C. D. Braun

from: J. Prakt. Chemie [Yearbook of Practical Chemistry] 96, 411-414 (1865)

Many years ago, Wöhler[1] demonstrated that during the action of ferrous sulfate on picric acid in the presence of an alkaline earth, picric acid is transformed into a new acid, which Berzelius named "nitro-hematic acid." Gerhardt remarked in his Traité de chimie organique, 3, 46: " Mr. Wöhler's nitro-hematic acid is probably impure picramic acid." The identity of this acid with picramic acid was

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[1] Berzelius' Jahresbericht, 9, 245 (1830).

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in fact confirmed a few years later by E. Pugh[1] and A. Girard[2]. In the same manner as ferrous sulfate (Wöhler), iron protochloride, stannous chloride or zinc (Pugh) and hydrogen sulfide in an alcoholic ammonia solution (Girard[3], C. Lea[4]) reduce picric acid to picramic acid, certain other substances also accomplish the same thing, as I confirmed for myself in a series of experiments. If, for example, one heats a solution of picric acid with potassium ferrocyanide solution, the fluid becomes cloudy at first from precipitating potassium picrate, but quickly clears as soon as one pours in some liquid ammonia. With further boiling, a deep red fluid ensues, developing from the picramic acid formed. If one performs the experiment in the same manner on potassium ferricyanide, then (as is to be expected) no reduction occurs; the yellow-colored fluid hardly changes its color. This relationship of potassium ferrocyanide to picric acid could provide a means for discriminating in some cases between ferrocyanic hydracid and ferricyanic hydracid, insofar as it might not be possible to use the usual reagents.

To a still much larger degree than potassium ferrocyanide, an alkaline glucose solution reacts with picric acid and produces even in moderately concentrated solutions an

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[1] Pogg. Journ. 65, 362. [2] Compt. rend. 42, 59.

[3] Compt. rend. 36, 421 and 42, 59.

[4] Sill. Americ. Journ. 31, 188 and 32, 211.

intensely blood-red fluid. If one heats glucose solution with potash lye or soda lye, with baryta water or lime water, or, finally, with a solution of sodium carbonate, one obtains (in not very concentrated solutions) a lemon-yellow fluid which transforms its color to a deep blood red when drops of picric acid solution are added and the mixture is once again heated to the boil. Of the aforementioned basic agents, potash lye and soda lye have the strongest effects; using ammonia I could not bring about the reduction of picric acid by glucose.

Pugh[1] found that during the reaction of ferrous oxide etc. (see above) on picric acid, picramic acid is formed according to the following equation:

$$C_6H_3X_2NO_2.O + 6Fe_2O + H_2O = C_6H_5X_2N.O + 3Fe_4O_3.$$ [2]

If one compares with this the reaction of potassium ferrocyanide in the presence of ammonia, then the process which here occurs can be expressed by the following formula:

$$C_6H_3X_2NO_2.O + 6K_4Fe_2Cy_6 + 3H_2O = C_6H_4KX_2N.O + 6K_3Fe_2Cy_6 + 4KHO.$$

Whether a usable method for production of the acid or, indeed, of potassium ferricyanide, can be based on the above, my further experiments will reveal. The metamorphosis of picric acid into picramic acid which occurs via glucose

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[1] loc. cit.

[2] $X = NO_2$

can quite probably be assumed as taking place in the following manner: Reichard[1] found that during the reaction of alkaline copper solution on glucose, gum and gummic acid are formed in addition to water, and I hypothesize the same products for the reaction of picric acid and grape sugar; more detailed experiments which I plan to undertake on the subject will, however, clarify the process further. According to the Trommer-Fehling-Bareswil method for sugar determination, as is well known, $2C_{12}H_{24}O_{12}$ reduces 20Mol. Cu_2O, takes up $5O_2$ in the process and transforms itself into the aforementioned substances. During the reaction of picric acid with glucose in an alkaline solution, 10Mol. ($C_6H_3X_2NO_2.O$) must accordingly lose $10O_2$ and with the cooperation of 10 Mol. water, 10 Mol. of picramic acid must develop, and subsequently gum and gummic acid.

$$10(C_6H_3X_2NO_2.O) + 10H_2 - 10(C_6H_5X_2N.O) = 10\ O_2,$$

$$4(C_{12}H_{24}O_{12}) + 10\ O_2 = 2C_{12}H_{26}O_{13} + 8C_3H_5O_5 + 2H_2O,$$

glucose. gum. gummic acid.

$$C_{12}H_{24}O_{12} + 5\ O_2 = 4C_3H_5O_5 + 2H_2O.$$

In all, therefore, 5 Mol. of glucose would be transformed into 2 Mol. of gum and 12 Mol. of gummic acid.

For the practical chemist, the relation of glucose to picric acid yields quite a useful reaction for the detection of glucose. In this, it is best to prepare a picric acid

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[1] Ann. d. Chem. u. Pharm. 127, 297.

solution of the concentration I use for the detection of prussic acid, so that there are 250 parts water to 1 part acid. One proceeds in the testing expediently by adding a few drops of picric acid to a glucose solution which has been mixed with some soda lye, and then heating the mixture to boiling. If the glucose solution was only somewhat concentrated, one will now obtain an intensely blood red fluid, while the color of thinner glucose solutions will be deep red. Since cane sugar does not demonstrate this behavior at all, the practician can derive from this a simple means to recognize the glucose in beet sugar and the like. For the practicing physician the new reaction will likewise be of interest to determine whether a questionable urine is diabetic or not. I had the opportunity on various occasions to test the urine of persons suffering from diabetes mellitus, and obtained by the above reaction a very bright red fluid. Like glucose, fructose and lactose also demonstrate this lovely reaction, but not cane sugar or mannitol.

Laboratory at Wiesbaden, October, 1865.